Supporting Information

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SI Text: Supporting Thermochemical Data

In ref. 1, $\Delta G^{\circ}_{acid}(HN(SO_2C_4F_9)_{2,})$ = 284.1 ± 2.0 kcal·mol^{-1} is provided, and it is noted that $T\Delta S_{acid}$ = 7 ± 0.8 kcal·mol^{-1} is generally applicable for the acids that were studied. We used this quantity to derive the value of $\Delta H^{\circ}_{acid}(HN(SO_2C_4F_9)_2)$ given in the text.

An alternative value of ΔH°_f(LiOH) = −54.7 ± 1.2 kcal·mol^{-1} has been reported (2), but the current quantity in the NIST database (3) was used because it is in better accord with a recommended value of −57.1 ± 1.2 kcal·mol^{-1} based on previous high-level computations (4) and the high-level theoretical predictions of −57.8 (W1), −57.2 (W2C), and −56.8 (CAS-AQCC/aug-cc-pVQZ) kcal·mol^{-1} in the present study.

D_0(Li—O$^{\cdot}$) = 87.6 kcal·mol^{-1} has been reported (5) and is in reasonable accord with crude estimates of 82 ± 4 (6) and 91 kcal·mol^{-1} (7). No experimental uncertainty was given for D_0, but a second less reliable measurement was provided in the same study that is 3 kcal·mol^{-1} larger. Our best calculations give a value of ≈84 kcal·mol^{-1}, so an uncertainty of ± 3.0 kcal·mol^{-1} was adopted. This bond energy was converted to 298 K by adding 0.9 kcal·mol^{-1} (3/2(RT)) and combined with ΔH°_f(Li) = 38.07 ± 0.24 kcal·mol^{-1} and ΔH°_f(O) = 59.555 ± 0.024 kcal·mol^{-1} (3) to obtain the heat of formation of LiO$^{\cdot}$. Other values based on appearance potential measurements made 35–50 years ago are considered to be unreliable (3, 8–10). This includes the heat of formation given in the NIST database (20.1 ± 5.1 kcal·mol^{-1}), which is the average of two measurements from one study [i.e., the mean of 13.7 ± 2.5 and 18.3 ± 5 kcal·mol^{-1} is 16.0 ± 5 kcal·mol^{-1} (9), but this value was subsequently modified upon a reevaluation of the poorly established auxiliary data].

1. Koppel IA, *et al.* (1994) The gas-phase acidities of very strong neutral Bronsted acids. *J Am Chem Soc* 116:3047–3057.
2. Gurvich LV, *et al.* (1996) Thermodynamic properties of alkali metal hydroxides. Part 1. Lithium and sodium hydroxides. *J Phys Chem Ref Data* 25:1211–1276.
3. Bartmess JE (2005) *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, eds Mallard WG, Linstrom PJ (National Institute of Standards and Technology, Gaithersburg, MD). Available at http://webbook.nist.gov.
4. Sullivan MB, *et al.* (2003) Heats of formation of alkali metal and alkaline earth metal oxides and hydroxides: Surprisingly demanding targets for high-level ab initio procedures. *J Phys Chem A* 107:5617–5630.
5. Woodward JR, Hayden JS, Gole JL (1989) Formation and characterization of a low-lying electronic state of the alkali monoxides LiO . . . CsO in the red and near infrared. *Chem Phys* 134:395–419.
6. Herm RR, Herschbach DR (1970) Molecular beam kinetics: Reactions of alkali atoms with NO_2 and CH_3NO_2. *J Chem Phys* 52:5783–5792.
7. Figger H, Schrepp W, Zhu X-h (1983) Chemiluminescent reaction between alkali dimers and oxygen molecules. *J Chem Phys* 79:1320–1325.
8. Berkowitz J, Chupka WA, Blue GD, Margrave JL (1959) Mass spectrometric study of the sublimation of lithium oxide. *J Phys Chem* 63:644–648.
9. White D, Seshadri KS, Dever DF, Mann DE, Linevsky MJ (1963) Infrared spectra and the structures and thermodynamics of gaseous LiO, Li_2O, and Li_2O_2. *J Chem Phys* 39:2463–2473.
10. Hildenbrand DL (1972) Thermochemistry of the molecular species LiO, LiO^+, and Li_2O^+. *J Chem Phys* 57:4556–4560.

Table S1. Relative energies of $LiCO_2^-$ isomers 1 and 2 and the EA(1) at various computational levels

Method	E_{Rel}, kcal·mol^{-1} 1 Singlet	1 Triplet	2 Singlet	2 Triplet	EA(**1**), eV
B3-LYP/6-311+G(2df,2pd)*	0.0	3.4	2.2	1.5	0.59
B3-LYP/AA′VTZ	0.0	3.7	2.4	2.2	
CCSD(T)/AA′VTZ†	0.0	4.7	3.0	4.5	0.49‡
W1	0.0	4.9	3.2	4.7	0.65§

All energies are at 298 K.

*Similar geometries are obtained with the AA′VTZ basis set in that all of the bond lengths are within 0.005 Å.

†These single-point energies were obtained by using the B3-LYP/AA′VTZ geometries and scaled zero-point energies and temperature corrections.

‡CCSD(T)/aug-cc-pVTZ energy.

§G3 energy.

Table S2. Computed energetic quantities for LiOH and LiO· at 298 K (kcal·mol^{-1})

	ΔH°_f(LiOH)	ΔH°_f(LiO·)	EA(LiO·)	BDE(LiO—H)	ΔH°_{acid}(LiOH)
B3LYP*	—†	—†	12.7	120.8	421.3
G3	−56.7	12.6	11.8	121.3	423.9
G4	−57.0	12.7	12.3	121.8	424.1
AQCC‡	−56.8	12.5	9.0	121.4	426.2
BD(T)§	—†	—†	9.8	121.1	425.0
W1	−57.8	12.4	9.9	122.4	426.3
W2C	−57.2	12.9	10.0	122.2	426.0

*B3-LYP/6-311+G(2df,2pd).
†Method not suitable for computing atomization energies.
‡CAS-AQCC/aug-cc-pVQZ.
§BD(T)/aug-cc-pVQZ.

Table S3. Computed B3-LYP/6-311+G(2df,2pd), G3, BD(T)/aug-cc-pVQZ, and CAS-AQCC/aug-cc-pVQZ acidities of HX at 298 K

	ΔH°_{acid}, kcal·mol^{-1}			
Compound	B3-LYP	G3	BD(T)	AQCC
$LiBH_2$	392.6	391.3*	395.1	393.7
$LiCH_3$	399.7	400.7	401.6	402.8
$LiNH_2$	410.3†	411.6	413.5	414.7
LiOH	421.3	423.9	425.0	426.2
LiSH	373.5	372.9	375.8	376.0
LiH	359.5	354.5	355.8	356.3
BeH_2	397.0	392.7	393.4	395.9
BH_3	411.9	413.5	412.1	412.2
CH_4	416.7	419.3	418.8	419.2
Li_2BH	387.8	386.0*	385.3	384.8
Li_2CH_2	397.6	397.0	399.8	400.1
Li_2NH	412.5	423.7	417.6	419.7
$NaCH_3$	401.1	401.6	401.2	402.0
NaOH	413.0	417.8	418.6	419.7
NaSH	377.8	379.1	382.0	381.5
NH_3	404.4	405.1	403.7	404.9
H_2O	390.7	391.4	390.4	394.1
HF	370.0	372.3	371.8	374.1

Interestingly, LiH, BeH_2, and BH_3 show the same trend with electronegativity as the lithiated species and the opposite relationship to the remaining first-row hydrides.

*G3B3 energy.

†A referee suggested that $LiNHCH_3$ be considered. We have calculated its B3-LYP acidity as 398.9 kcal·mol^{-1}; i.e., it does not compete with LiOH as the weakest acid.